

Defending against Corrosion

A Livermore-designed engineered barrier system for the proposed Yucca Mountain nuclear waste repository works with natural barriers to keep radioactive waste in its place.

Years of scientific study have been devoted to designing a proposed underground nuclear waste repository at Yucca Mountain in the Nevada desert.

Lawrence Livermore National Laboratory

LAURENCE Livermore researchers thrive on challenging assignments. Few assignments have been as demanding as designing a waste package system to keep high-level radioactive waste packages essentially intact for at least 10,000 years. A team of Livermore researchers—engineers, metallurgists, chemists, microbiologists, and computer scientists—are testing and refining the design and materials for what will eventually be 12,000 waste packages. These efforts are an integral part of a national program to design, license, and build an underground nuclear waste repository in Yucca Mountain, Nevada.

Yucca Mountain was selected by the Department of Energy (DOE) as a highly promising repository site. (See the [box on](#)

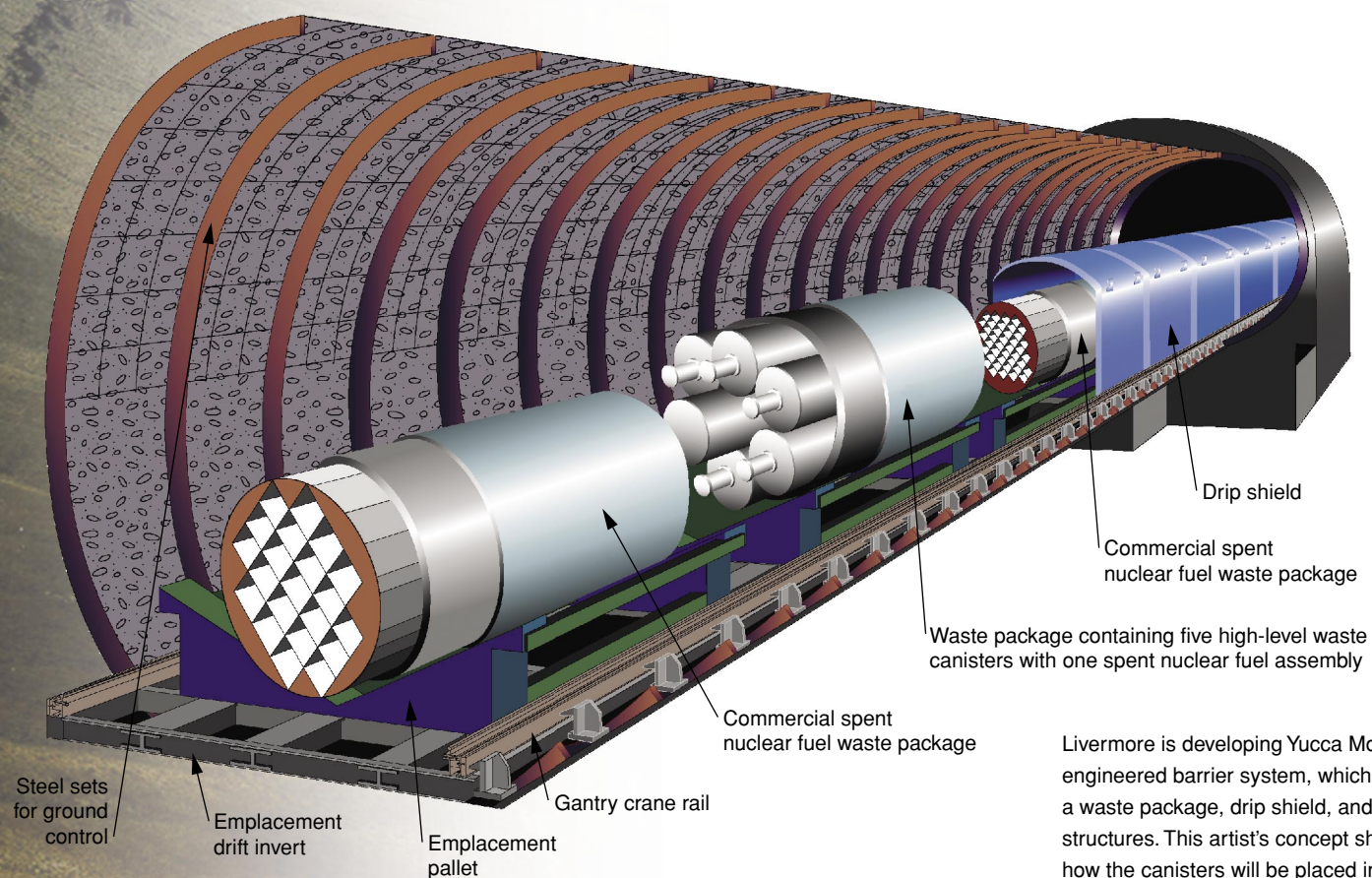
p. 14.) In 1987, Congress directed the DOE to focus on Yucca Mountain as the candidate location to safely store about 70,000 tons of waste from civilian nuclear power plants and highly radioactive waste from defense-related activities at DOE facilities. As part of the DOE's Yucca Mountain Project, Livermore scientists have made major contributions in characterizing the proposed underground site, determining the effects on the site from storing high-temperature radioactive wastes, and selecting and characterizing corrosion-resistant materials.

Livermore's largest effort is developing Yucca Mountain's engineered barrier system, which consists of a waste package, drip shield, and supporting structures. The engineered barrier system is designed to

work with the natural barriers of Yucca Mountain to contain the repository's radioactive wastes and prevent them from seeping into the water table which lies about 300 meters below the planned repository.

"We need to show that our design will substantially contain the waste inside the canisters for at least 10,000 years under extreme and varying conditions of temperature, radiation, and corrosion," says Dan McCright, Livermore metallurgist and Yucca Mountain Program senior scientist. According to McCright extensive analyses have shown that even if waste were to eventually leak from the canisters, additional barriers, both natural and engineered, are expected to keep the waste far from the water table and humans.

No direct information exists about how modern materials will behave over thousands



Livermore is developing Yucca Mountain's engineered barrier system, which consists of a waste package, drip shield, and supporting structures. This artist's concept shows how the canisters will be placed in tunnels about 300 meters underground. The waste packages will rest on a strong corrosion-resistant pallet and supporting steel frame.

of years under a range of conditions. The Livermore research is based on accelerated aging tests of materials that are proposed to make up the engineered barrier system and on computer models that simulate how a repository built at Yucca Mountain would perform over thousands of years.

Defense in Depth

The current repository design calls for waste to be stored in a package consisting of a set of two nested canisters—an outer canister made of a highly corrosion-resistant metal (Alloy 22) and an inner canister made of a tough, nuclear-grade stainless steel (316NG). An overhanging drip shield made of titanium will provide additional protection to the waste package from dripping water and any falling rocks from the repository ceiling. “Because the waste package and the drip shield are made of different corrosion-resistant materials, they form corrosion defense in depth,” says McCright.

Storing the waste packages horizontally and commingling the different kinds of

waste packages will create a relatively uniform temperature in each underground drift, or tunnel, carved inside the mountain. The waste packages have a common diameter (1.8 meters), but their lengths vary according to the type of waste—from about 3.6 meters for the defense waste to 5.7 meters for the spent nuclear fuel.

The most critical element of the engineered barrier system is the 20-millimeter-thick outer canister made of Alloy 22, which consists of about 60 percent nickel, 22 percent chromium, 13 percent molybdenum, and 3 percent tungsten. Alloy 22 is highly resistant to fractures and is easier to weld than alternative materials such as titanium. It is also extremely corrosion resistant under the conditions of high temperature and low humidity expected to prevail for hundreds to thousands of years in a repository. In addition, it is resistant under conditions of either low or high humidity at the lower temperatures expected in the repository when radiation levels decrease. Hence, the

selection of Alloy 22 would provide containment over a range of environmental conditions. “It’s the best engineered material available for the job,” says McCright.

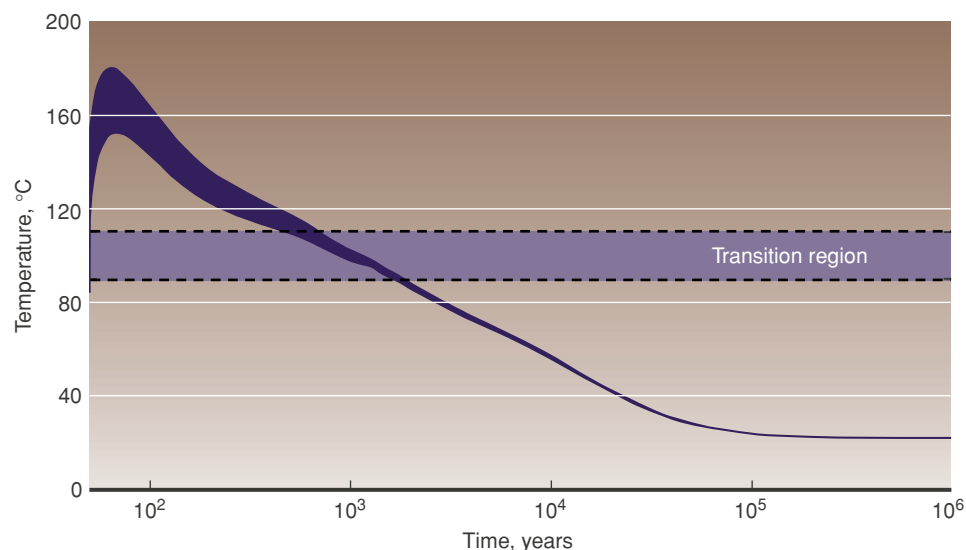
Nuclear-grade stainless steel (316NG) was chosen for the 50-millimeter-thick inner canister to add strength and bulk to the waste package. It is corrosion resistant, more compatible with Alloy 22 than carbon steel, and more economical than more complex steel alloys.

The titanium drip shield, which McCright compares to a sturdy awning, would be fabricated from grade 7 titanium. This material contains a small amount of palladium to provide greater corrosion resistance. The drip shield, however, is not considered essential to containing the wastes. Earlier projections of Alloy 22’s corrosion performance assumed that there would be no drip shields and that drips from the repository walls would fall directly on the canisters.

The waste packages will rest on a pallet fabricated from Alloy 22 clad onto steel.



Livermore scientists are testing the design of the waste packages to be used in the Yucca Mountain repository. The waste packages will have a common diameter (1.8 meters), but their lengths will vary according to the type of waste—from about 3.6 meters for defense waste to 5.7 meters for spent nuclear fuel. The scientists work on prototypes like the one above that have the full-scale diameter but shortened lengths.



Once the repository is sealed, it will take hundreds of years before waste-package surface temperatures drop below boiling because of the slow decay of the radioactive waste. This graph shows the projected decline of temperatures on waste canisters’ surfaces over 1 million years. The range of temperatures corresponds to uncertainty about heat-transfer modes, variation among the heat output of individual waste packages, and the location of waste packages in the repository. The dotted transition region marks where temperatures fall below boiling. At this point, water may come into contact with the containers.

The pallet, in turn, will sit on a steel frame and crushed gravel. The waste packages will be placed close together (about a meter apart) so that by design their surfaces will reach a maximum surface temperature of 160°C (caused by radiation levels of up to 180 rads per hour) once the repository is sealed. "It may take hundreds of years before surface temperatures cool below boiling because of the slow decay of radioactive components in the waste," says McCright. Keeping the canister surfaces above the boiling point will ensure they are dry, with the intention to prevent corrosion.

Getting a Close-up View

A major effort is under way to understand and characterize the environments closest to the drip shield and the waste package because these environments will determine the potential for corrosion and how fast it could proceed. Surface conditions will be characterized by the temperature, humidity, and composition of gases in the repository; the contaminants in the dripping water from repository walls; and the mixture of minerals and salts that may eventually be deposited on the drip shield and canisters. As temperatures cool, for example, moisture and dust in the atmosphere will settle on the canisters' surfaces despite the presence of the drip shield. If a drip shield is eventually breached, water seeping through rock fissures could contact the canisters directly and cause more minerals or salts to precipitate on their surfaces, thereby increasing the potential for corrosion.

Limiting corrosion is the paramount objective. Corrosion can be general, occurring more or less uniformly over the entire surface, or localized, occurring in specific areas such as in pits or crevices on a metal's surface. Corrosion can also be assisted by cracking from stresses in a metal or weld, a phenomenon called stress corrosion cracking.

The materials chosen for the waste package are among the most corrosion resistant of engineering materials. They are used routinely under harsh conditions in the

chemical process industry and at nuclear power plants and are expected to perform well in the expectedly more benign conditions within Yucca Mountain. Both titanium and Alloy 22 gain their corrosion protection from the natural, extremely fast growth of thin films (about 3.5 nanometers or 10 atomic layers thick) of metal oxides caused by oxygen in the environment. When these stable, chemically unreactive films consolidate, the corrosion rate decreases. One Livermore research effort is studying the growth of metal-oxide thin films on Alloy 22 and titanium under the expected environmental scenarios at Yucca Mountain. The observed compositions and structures of the films are compared with model predictions of film growth.

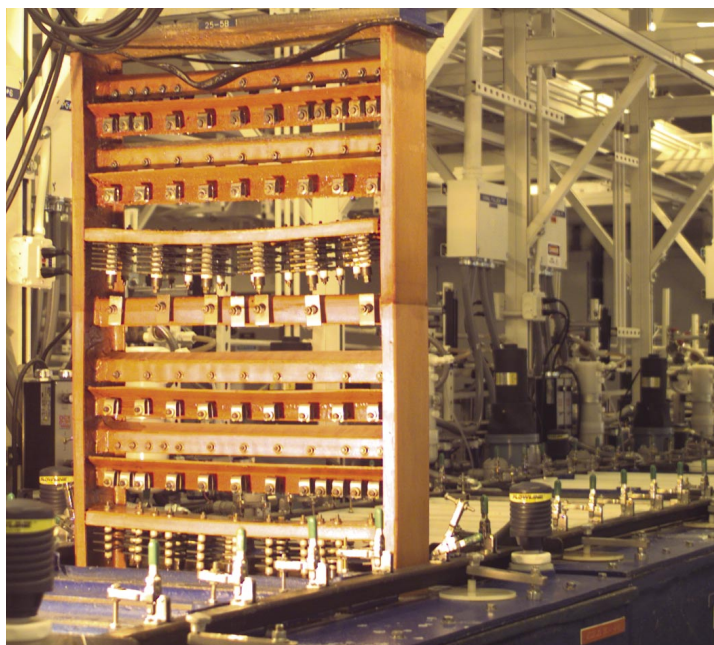
It is essential to demonstrate that Alloy 22 will survive all anticipated repository conditions. In particular, scientists must show that corrosion rates, both general and localized, are extremely low and that welds will not crack over time. Materials performance tests are conducted at Livermore's Long-Term Corrosion Test Facility (LTCTF) to provide assurance that the waste packages will maintain their

integrity and corrosion resistance for thousands of years.

Aging 18,000 Metal Coupons

The corrosion tests at the LTCTF are designed to rapidly "age" metal samples, called coupons, by subjecting them to much harsher conditions than would be expected in the repository. More than 18,000 alloy coupons are being tested, each of which measures about 5 centimeters square or less. Fourteen alloys are being tested to compare the corrosion resistance of Alloy 22, stainless steel, and titanium with other materials.

Four kinds of coupons are used to test the various forms of corrosion. Crevice coupons consist of metals tightly pressed against Teflon washers to determine the extent of corrosion from liquid trapped between the metal and washer. Weight-loss coupons measure general corrosion. Galvanic coupons measure corrosion that occurs when two dissimilar alloys are pressed against each other. Finally, U-bend coupons are metals bent under continuous stress to try to induce stress corrosion cracking. Many of the coupons are welded to determine the effects, if any, of welds on corrosion.



Corrosion tests of metal samples, called coupons, are carried out at Livermore's Long-Term Corrosion Test Facility. Four types of coupons are kept in 24 tanks, each filled with about 1,000 liters of one of the three aqueous solutions that are likely to be found in the underground Yucca Mountain environment. In this photograph, a rack containing several hundred coupons is pulled out of solution for inspection.

The coupons are kept in 24 tanks, each filled with about 1,000 liters of one of three different solutions derived from those likely to be found in the Yucca Mountain environment. One solution is a concentrated mixture of salts and minerals common to Yucca Mountain. The second solution is a diluted version of this mixture. The third

solution is an acidified version of the concentrated mixture. Solutions are heated to either 60°C or 90°C. The coupons are mounted on vertical racks and are either submerged in solution, suspended over the solution, or partially submerged.

Coupons were removed from the tanks six months, one year, two years, and five

years after mounting. (Most of the coupons are still in the tanks awaiting longer-term tests.) When a coupon is removed, it is analyzed to determine whether corrosion has occurred, and if so, where it is, and how much damage it caused.

Corrosion activity is evaluated by weighing the coupons after they are cleaned

Yucca Mountain Project Eyes Licensing

In 1982, Congress passed the Nuclear Waste Policy Act, which made the Department of Energy (DOE) responsible for finding a suitable site and designing, building, and operating a permanent underground radioactive-waste disposal facility, called a geologic repository. The search identified several possible locations for the nation's first long-term waste repository. In 1987, Congress amended its earlier act to focus solely on the Yucca Mountain site in Nevada, about 145 kilometers northwest of Las Vegas. On July 23, 2002, President George W. Bush signed House Joint Resolution 87, allowing DOE to proceed in establishing a safe repository in which to store nuclear waste.

Yucca Mountain is located in a remote desert on federally protected land within the secure boundaries of DOE's Nevada Test Site. Hundreds of scientists and engineers have studied Yucca Mountain's geology, hydrology, chemistry, climate, and other physical aspects that could affect a repository's safety. The U.S. is not the only country facing the disposal issue. Around the globe, virtually all nations that use nuclear power are exploring approaches to safely dispose of radioactive waste.

DOE is preparing an application to obtain a Nuclear Regulatory Commission license to proceed with construction of the repository. DOE has set 2010 as Yucca Mountain's opening date, that is, when the first waste will be placed in canisters and moved inside.

The Yucca Mountain repository would house more than 70,000 metric tons of spent nuclear fuel from civilian nuclear power plants and highly radioactive waste from defense-related activities at DOE facilities across the U.S. Currently, spent nuclear fuel is stored in ponds or silos near operating commercial nuclear plants, while high-level nuclear waste from defense programs and experimental reactors is stored as liquid in tanks or as glass logs at several DOE facilities.

Homeland Security Concerns

The vulnerability of this waste, dispersed in so many locations, to potential terrorists is of concern to homeland security experts. The government's plan is to dispose of this waste in a centralized, well-monitored, and highly secure repository.

Nearly 90 percent of the waste will be spent fuel, which consists of solid pellets of enriched uranium oxide sealed in a cladding of corrosion- and heat-resistant zirconium alloy. The spent nuclear fuel from power plants would be delivered to the Yucca Mountain site "as is." The waste from DOE defense programs would first be vitrified, that is, converted into a borosilicate glass, before delivery to the repository.

The Yucca Mountain repository would be constructed in a layer of rock called tuff about 300 meters below the surface and about

300 meters above the permanent water table. Yucca Mountain is unique among potential sites under consideration in the waste disposal programs throughout the world because waste would be emplaced above the water table in an environment that is oxidizing in nature (that is, has plenty of oxygen).

Applying the principle of "defense in depth," the repository would incorporate multiple protective barriers, both natural and engineered. The engineered barriers include a canister and an overhanging drip shield. Emplaced waste would be monitored for the first 100 years of operation, and then the repository would be permanently closed. Scientists believe the dry conditions within the tuff will minimize the prospects for water to contact the canisters and that the waste will be sufficiently isolated for thousands of years.

The Yucca Mountain Project falls under the purview of the DOE Office of Civilian Radioactive Waste Management. The prime contractor is Bechtel SAIC Company, LLC, which is a joint venture between Bechtel National and Science Applications International Corporation. The project is one of the most closely reviewed programs ever undertaken by the federal government. Reviewing organizations include Congress, the General Accounting Office, the Nuclear Regulatory Commission, the State of Nevada's Nuclear Waste Project Office, Nye County Nuclear Waste Repository Office, the Nuclear Waste Technical Review Board, and the National Academy of Sciences.



Scientists at Yucca Mountain's Drift Scale Test Facility are acquiring a better understanding of the thermal, mechanical, hydrological, and chemical processes that occur deep underground at the site.

of compounds that have precipitated on their surfaces and by using an electron microscope and an atomic force microscope to scrutinize their surfaces.

LTCTF manager Dave Fix notes that the corrosion detected in the coupons in the various solutions is generally so slight that it resides at the limit of what is measurable. The average corrosion rate is about 20 nanometers per year. At this rate, a 20-millimeter-thick barrier of Alloy 22 would be effective for more than 100,000 years before general corrosion would provide a means for water to contact the underlying stainless-steel layer. In addition, the extremely low corrosion rates appear to be nearly the same for all the water chemistries and temperatures tested.

Significant corrosion is measured only when coupons are subjected to extreme, unrealistic conditions. For example, the basic metallurgical structure of Alloy 22 is transformed over long periods of time at temperatures of more than 500°C (100°C is the boiling point of water at sea level). Several hundred millivolts of electrochemical potential are necessary to make the test solution extremely corrosive. "These extreme testing conditions are totally unrealistic for the Yucca Mountain repository setting," says McCright, "but our models consider them."

Assessing Microbes' Effects

Livermore microbiologist Joanne Horn leads a team assessing the potential damage microbes can cause to the engineered barrier system. Some bacteria and fungi, both those indigenous to Yucca Mountain and those introduced by construction activities, could cause corrosion of the engineered barriers. Horn notes that an abundance of microbes exists in the Yucca Mountain repository setting. Microbial activity is expected on the canisters when adequate moisture is present. Some bacteria, for example, are expected to form patchy, thin films over the metal-oxide films covering the waste packages and drip shields.

Horn notes that microbes have been found in the most inhospitable environments on Earth, such as the scalding vents at the

ocean's floor. Some bacteria have very efficient DNA repair mechanisms that might enable them to survive high radiation levels.

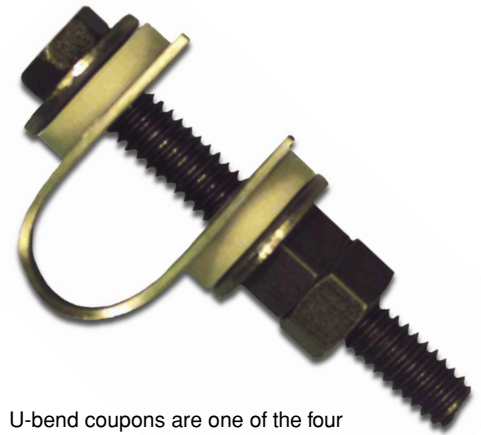
Horn's team has identified more than 65 species and subspecies of bacteria living in the Yucca Mountain rock. The team has also identified the different growth requirements for these bacteria. One set of laboratory experiments analyzes the extent of corrosion on metal coupons caused by bacteria contained in crushed Yucca Mountain rock and fed with simulated groundwater. Another set of experiments determines the extent of corrosion caused by specific species of bacteria that have potentially corrosive activities, such as a species that oxidizes sulfur compounds. The results of these experiments are compared with the corrosion that occurs under identical conditions but in environments that have been presterilized to kill all microbes. The team also analyzes the solutions to determine if bacterial metabolic products could change the repository chemistry.

"The findings of the bacterial experiments parallel those of the long-term corrosion facility," says Horn. "To date, our results show that over 10,000 years, the corrosion rate from bacteria would not penetrate beyond 1 millimeter. Alloy 22 is a very tough metal."

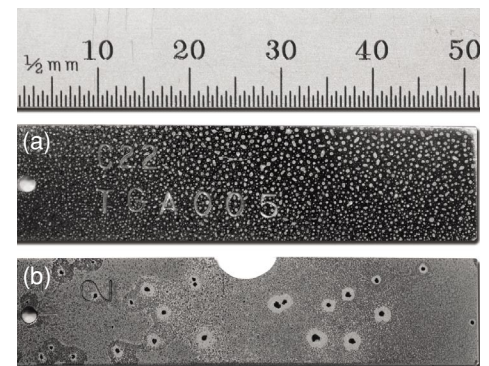
Overcoming Weld Stresses

How the waste packages are manufactured, especially the required welds, can affect their resistance to corrosion as well as their structural integrity. Residual stresses are a common by-product of manufacturing, especially welding, and if left untreated could lead to stress corrosion cracking. Livermore metallurgists plan to treat the canister welds in the repository with an annealing process that reduces the residual tensile stress and produces instead a compressive stress on the canisters' surface. Stress corrosion cracking does not occur under compressive stress.

The annealing process involves subjecting the welds to 1,100°C and then quenching



U-bend coupons are one of the four types of coupons being tested for corrosion resistance. U-bends are metals kept under continuous stress to try to induce stress corrosion cracking.



Coupons of (a) Alloy 22 and (b) Alloy 825 (which contains less nickel and molybdenum than Alloy 22) show many precipitates when subjected to high concentrations of minerals and salts. However, Alloy 22 has no localized corrosion whereas Alloy 825 has permanent pits caused by corrosion.

the metal in a water bath to produce a small overall compressive stress on the exterior surface. The canisters would then be shipped from the factory to the repository for storage until they are ready to be filled and sealed.

The canister lids would be fabricated offsite and then welded on after the canister was filled at the repository. Annealing would not work as a technique to lessen the stresses that will unavoidably occur in the final closure welds because the high heat generated during the process would damage the contents. "The nuclear waste will be in a relatively inert form when it is placed in the canisters," says McCright. "Subjecting the waste to the temperatures required by annealing might compromise that inertness."

One promising alternative to annealing is laser peening, a process developed at Livermore, in which a laser produces a shock wave on a weld to form a compressive stress. (See *S&TR*, March 2001, pp. 26–28.) Laser peening can produce a compressive layer about 3 millimeters deep in the metal to strengthen the final closure welds. Livermore experts are characterizing structural changes of peened Alloy 22 samples using transmission electron microscopy, x-ray diffraction, and other techniques.

Favorable Testing Results

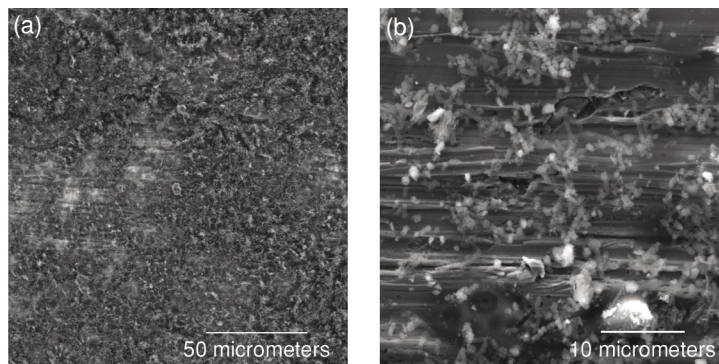
Attempts to accelerate corrosion with solutions representing the waters that could eventually contact the metal canisters have thus far indicated an extremely low general

corrosion rate. The tests also have shown that the canister metals have extremely high resistance to all forms of localized corrosion and stress corrosion cracking in environments relevant to the repository. Also, no appreciable differences have been noted in corrosion rates obtained from the various water compositions and temperatures. The testing results support Livermore's models for long-term prediction of the waste packages' performance and strongly confirm the selection of Alloy 22 for the outer canister.

Testing and modeling at Livermore will proceed for several more years. In the meantime, McCright and others are refining the engineered barrier design to make components more efficient and economical to manufacture. "The plan is to manufacture 12,000 waste packages over 25 years, the equivalent of manufacturing more than one canister a day," he says. "We want every one to be as corrosion resistant as we can practically make them."

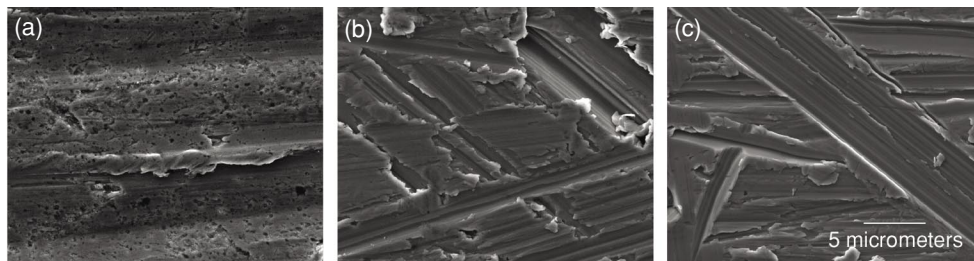
—Arnie Heller

Thin films of bacteria form on the surface of metal coupons tested in a solution containing nonsterile crushed Yucca Mountain rock. Bacteria that have colonized on an Alloy 22 coupon are shown magnified (a) 1,200 times and (b) 5,000 times.



Key Words: Alloy 22, engineered barrier system, laser peening, Long-Term Corrosion Test Facility (LTCTF), Nevada Test Site, Nuclear Regulatory Commission, nuclear waste repository, Yucca Mountain.

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Electron micrographs (8,000 times magnification) show the extremely limited corrosion on an Alloy 22 coupon caused by bacteria after (a) 57 months in a solution containing nonsterile crushed Yucca Mountain rock compared to (b) a coupon that has been in a solution with presterilized rock (to kill all microbes) for 43 months, and (c) the same coupon at the start of the experiment.